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(54) Title: STABILIZER COMPOSITIONS FOR HALOGEN-CONTAINING POLYMERS AND POLYMER COMPOSITIONS CONTAINING SAME

(57) Abstract

A stabilizer composition for use in halogen-containing polymers comprising hydrotalcite and a molecular-sieve zeolite.

STABILIZER COMPOSITIONS FOR HALOGEN-CONTAINING POLYMERS AND POLYMER COMPOSITIONS CONTAINING SAME

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to stabilizer compositions for halogen containing polymers, particularly polymers of vinyl chloride, and to polymeric formulations containing such compositions.

2. Background of the Invention

Halogen-containing polymers, more general by vinyl chloride polymers (PVC), are commonly used for wire insulation and cable jacketing purposes, particularly for use in office buildings and the like. In order to impart thermal stability to PVC insulation and/or cable jacketing, various thermal stabilizers are incorporated. In particular, lead salts have been used as thermal stabilizers in such PVC formulations. Along with providing heat stability, lead based stabilizers generally impart good electrical insulating properties to the polymeric formulation.

Because of increasing health and environmental concerns, attempts have been made to replace the lead based thermal stabilizers in PVC and other halogen-containing polymeric compositions. For example, a common PVC heat stabilizer comprises a mixture of antimony and tin salts. While these stabilizers are preferable to lead based stabilizers from a health and environmental viewpoint, they generally do not provide the electrical insulating properties which can be achieved using lead based thermal stabilizers.

Ideally, a thermal stabilizer for halogen-containing polymeric composition would contain no heavy metal salts, e.g. lead salts, but would impart thermal stability and electrical insulating properties equivalent or superior to those achieved with lead salts.

SUMMARY OF THE INVENTION

It is therefore an object of the present invention to provide an improved stabilizer composition for use in halogen-containing polymers.

Another object of the present invention is to provide a stabilizer composition for halogen-containing polymers which eliminates the use of salts of heavy metals.

Still another object of the present invention is to provide a halogen-containing polymeric composition containing a thermal stabilizer which is free of heavy metal salts.

The above and other objects of the present invention will become apparent from the description given herein and the claims.

In one aspect, the present invention provides a stabilizer composition for use in halogen-containing polymers comprising a hydrotalcite having the general formula:

$$Mg_{1-x}Al_x(OH)_2A_{x/2}.mH_2O$$

wherein x is a number from 0 to 0.5, A is CO_3^- or SO_4^- and, M is a number representing the number of H_2O in the molecule, and a molecular-sieve zeolite having the general formula:

$$M_{2/n}0.Al_20_3.ySi0_2wH_20$$

wherein M is a cation of a metal selected from Group IA and Group IIA elements, y is 2 or greater, n is the cation valence, and w represents the water contained in the voids of the zeolite, the ratio Si/Al in the zeolite being greater than about 1, the weight ratio of hydrotalcite to zeolite being from about 0.5 to 1 to about 3 to 1.

In another aspect of the present invention, there is provided a composition of a halogen-containing polymer and an effective amount of the stabilizer composition described above.

DESCRIPTION PREFERRED EMBODIMENTS

The stabilizer composition of the present invention comprises two main ingredience (1) a hydrotalcite, and (2) a molecular-sieve zeolite. The hydrotalcite used in the stabilizer composition of the present has the general formula:

$$Mg_{1-x}Al_x(OH)_2A_{x/2}.mH_2O$$

wherein x is a number from 0 to 0.5, A is CO_3^- or SO_4^- and, m is a number representing the number of H_2O in the molecule. The hydrotalcites which can be used includes the various naturally occurring mineral hydrotalcites and synthetic hydrotalcites falling within the above described formula. Such hydrotalcites can be used in the form of their higher fatty acid alkali metal salts or organic sulfonic acid alkali metal salts. Especially preferred are the hydrotalcites wherein x is a number from about 0.1 to about 0.4, A is CO_3^-, and m is from about 0.4 to about 0.7, e.g. x is 0.33, A is CO_3-- -- and m is 0.5.

The other main component of the stabilizer composition is a molecular-sieve zeolite having the general formula:

$$M_{2/n}0.Al_20_3.ySi0_2wH_20$$

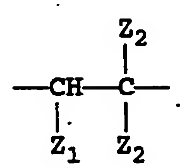
wherein M is a cation of a metal selected from Group IA and Group IIA elements, y is 2 or greater, n is the cation valence, and w represents the water contained in the voids of the zeolite, the ratio Si/Al in the zeolite being greater than about 1. It is preferred that the zeolite be of a type which has an average pore size of greater than about 5 Angstroms, preferably greater than about 10 Angstroms. It is also preferred that an X zeolite be employed rather than an A zeolite. Also preferred, although not necessary is that the cation M be an alkali metal, particularly sodium. For a discussion of zeolites useful in the compositions of the present invention, reference is made to ENCYCLOPEDIA OF CHEMICAL TECHNOLOGY, 1981 Vol. 15, Pp 638-653 (herein incorporated by reference for all purposes).

The hydrotalcite and zeolite will be used in the stabilizer composition such that the weight ratio of hydrotalcite to zeolite is from about 0.5 to 1 to about 3 to 1.

In addition to hydrotalcite and zeolite, the stabilizer compositions of the present invention can also contain, with advantage, a beta-diketone. As disclosed in U.S. Patent 4,427,816, beta-diketones and hydrotalcite can be used advantageously as stabilizer compositions in halogen-containing polymers to enhance resistance to

heat and light deterioration of the polymers. The beta-diketones which are useful in the compositions of the present invention are disclosed and claimed in U.S. Patent 4,427,816, herein incorporated for reference for all purposes. In particular, the beta-diketones useful are described in column 2, line 11 - column 3, line 6 of U.S. Patent 4,427,816. When employed, the beta-diketone will be present in the stabilizer composition, in an effective amount, and will generally constitute from about 1 to about 15 percent by weight of the stabilizer composition.

The stabilizer compositions of the present invention are advantageously used in polyvinyl halide resin compositions comprising a polyvinyl halide resin formed at least in part of the re-occurring group



having a halogen content in excess of 40 percent by weight, wherein Z is halogen and Z_2 is either halogen or hydrogen. They are particularly useful in PVC compositions, e.g., either homopolymers of vinyl chloride or copolymers of vinyl chloride and at least one other copolymerizable monomer. In general, the stabilizer compositions of the present invention, when used in such halogen containing polymers, will be present in an effective amount, i.e., an amount sufficient to impart sufficient thermal stability and satisfactory electrical insulating properties. More generally, the stabilizer composition will be present in such halogen containing polymeric resins in an amount of from about 0.5 to about 10 parts per hundred parts of resin (phr).

As the data presented hereafter shows, the use of hydrotalcite and zeolite, in general, provides synergistic results in terms of electrical insulating properties, particularly properties such as volume resistivity (VR).

To more fully illustrate the present invention, the following non-limiting examples are presented. In all cases, the compositions are shown in terms of parts per hundred parts of resin (phr).

EXAMPLE 1

Brabender stability testing was conducted on a series of PVC resin

formulations. The base resin formulation was as follows:

INGREDIENT	PHR
PVC Resin	100.0
Trioctyl trimellitate	48.0
Paraffin wax	0.2
Ca CO_3	8.0
Clay	16.0
Antimony oxide	3.0

The base formulation was admixed with various stabilizer compositions to formulate various stabilized PVC formulations. The compositions of the stabilized PVC formulations are shown in Table 1 below.

Table 1

Ingredient	Control	601-171A	601-171B	601-171B1	601-171C
ESO	——	5.0	5.0	5.0	5.0
Zn stearate	——	0.5	0.5	0.5	——
Ca stearate	——	1.5	1.5	1.5	——
Alcamizer 1[1]	——	1.0	0.5	1.0	——
13X zeolite[2]	——	——	0.5	0.5	——
Rhodiastab 83[3]	——	0.1	0.1	0.1	——
Topanol CA[4]	——	0.1	0.1	0.1	——
RUP - 14[5]	——	——	——	——	3.2
Halbase100EP[6]	3.0	——	——	——	——
Dythal XL[7]	3.0	——	——	——	——

[1] Hydrotalcite having the formula $Mg_{0.67}Al_{0.33}(OH)_2(CO_3)_{0.16}\cdot0.5H_2O$ marketed by Kyowa Chemical Industry Co., Ltd.

[2] Molecular-sieve zeolite (average pore size ~ 13 Angstroms) marketed by UOP.

[3] Dibenzoyl methane marketed by Rhône-Poulenc.

[4] 1,1,3-Tris(2-methyl-4-hydroxy-5-t-butyl phenyl)butane anti-oxidant marketed by ICI Specialty Chemicals.

[5] Barium/zinc stabilizer marketed by Adeka Argus Chemical Co., Ltd.

[6] Tribasic lead sulfate marketed by Halstab.

[7] Dibasic lead phthalate marketed by Anzon.

The stabilized compositions of table 1 were subjected to Brabender stability testing under the following conditions: 500 head, 200° C, 100 rpm, 68 g charge. The results are shown in Table 2 below.

Table 2

FORMULATION	DEGRADATION TIME (min)[a]	EQUILIBRIUM TORQUE(m-gm)	EQUILIBRIUM TEMP. (°C)
Control	31.3	368	218
601-171A	32.4	265	216
601-171B	33.2	305	214
601-171B-1	37.4	272	215
601-171C	38.2	275	214

[a] Average of two measurements

As can be seen from the data in Table 2, PVC formulations containing the hydrotalcite/zeolite stabilizer compositions of the present invention compare favorably, in terms of thermal stability, with PVC formulations containing only a lead based stabilizer.

EXAMPLE 2

In this example, a series of stabilized PVC formulations was made from a base formulation and various stabilizer compositions and the stabilized PVC formulations subjected to METS-IR testing. METS-IR testing involves molding a PVC sheet around a flat metal electrode and placing the specimen in a constant temperature water bath. The electrical resistance of the composition is then determined and is correlatable to on-wire insulation resistance measurements. The test is based in part an Underwriter's Laboratories Subject 1581 for insulation resistance properties.

The base PVC formulation had the following composition:

INGREDIENT	PHR
PVC resin	100.0
Trioctyl trimellitate	46.0
Clay	7.0
Paraffin wax	0.3

In the case of the PVC formulation without any lead stabilizer, the base formulation also contained the following:

INGREDIENT	PHR
ESO (epoxidized soybean oil)	3.0
Ca stearate	1.5
Zn stearate	0.5

Table 3 below shows the results of the METS-IR testing on various PVC formulations made with various stabilizers.

Table 3

Formulation	Stabilizer	phr	METS-IR (Mohms/1000 ft.)
A	Dythal XL	7.0	5402.7
B	DHT-4A-2[1]	1.0	5409.3
C	DHT-4A-2 Rhodiastab 83	1.0 0.22	3543.6
D	NaX zeolite[2]	1.0	3469.8
E	DHT-4A-2 NaX zeolite	1.0 1.0	6266.6

As can be seen from the data in Table 3, the combination of zeolite and hydrotalcite provides excellent METS-IR results as compared with hydrotalcite alone, zeolite alone or hydrotalcite and a beta-diketone.

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[1] Anhydrous hydrotalcite having the formula $Mg_{0.67}Al_{0.33}(OH)_2(CO_3)_{0.16}$ marketed by Kyoma Chemical Industry Co., Ltd.

[2] Molecular-sieve zeolite (average pore size ~ 13 Angstroms) marketed by UOP.

EXAMPLE 3

Volume resistivity measurements were conducted on a series of PVC formulations using lead stabilization, the stabilizer disclosed in U.S. Patent 4,427,816 and the stabilizer compositions of the present invention. To prepare the stabilized PVC formulations, the following base formulation was employed:

INGREDIENT	PHR
PVC resin	100.0
Dioctyl phthalate (DOP)	50.0
Zn stearate	0.3
Ca stearate	0.7

Using the base formulation, stabilized PVC formulations were prepared using various stabilizer composition. The compositions of the stabilized PVC formulations and VR measurement results are shown in Table 4 below.

Table 4

Formulation	Stabilizer	phr	VR ($x10^{13}$) lab
A	Alcamizer 1	1.05	1.7
B	Alcamizer 1 Rhodiastab 83	1.0 0.05	1.85
C	NaX zeolite	1.05	1.24
D	NaX zeolite Rhodiastab 83	1.0 0.05	0.95
E	Alcamizer 1 NaX zeolite	0.525 0.525	3.19
F	Alcamizer 1 NaX zeolite Rhodiastab 83	0.5 0.5 0.05	2.74
G	Dythal XL	7.0	1.58

EXAMPLE 4

A series of stabilized PVC formulations were prepared using various stabilizer compositions and VR data obtained on each of the stabilized formulations. In preparing the stabilized formulations, the following base formulation was employed:

INGREDIENT	PHR
PVC resin	100.0
DOP	45.0
Zn stearate	0.25
Ca stearate	0.75

The compositions of the various stabilized formulations and VR measurements are shown in Table 5 below.

Table 5

Formulation	Stabilizer	VR (ohms-cm) X 10^{13}
Comparative*	None	1.186
147B	Alzamizer 1(Alc1)	3.253
141B	"	3.251
84B	"	5.310
104B	4A Zeolite[1] (4A)	1.265
104C	5A Zeolite[2] (5A)	1.353
84C	NaX Zeolite	3.480
84D	Rhodiastab 83 (Rho 83)	0.1937
147C	Alc 1/Rho 83	4.082
141C	Alc 1/Rho 83	2.910
84E	Alc 1/Rho 83	4.469
141D	Alc 1/4A	3.593
104H	Alc 1/4A	3.083
141E	Alc 1/5A	3.190
104I	Alc 1/5A	2.919
141F	Alc 1/3A Zeolite[3] (3A)	2.532
141G	Alc 1/13X	5.260
84H	Alc 1/NaX	11.67
104D	4A/Rho 83	0.2874
104E	5A/Rho 83	0.6930
84F	NaX/Rho 83	2.260

* Average of four samples

[1] Molecular-sieve zeolite (average pore size ~ 4 Angstroms) marketed by Zeochem.

[2] Molecular-sieve zeolite (average pore size ~ 5 Angstroms) marketed by Zeochem.

[3] Molecular-sieve zeolite (average pore size ~ 3 Ångstroms) marketed by UOP.

TABLE 5 (con't)

147D	Alc 1/4A/Rho 83	4.087
104F	Alc 1/4A/Rho 83	2.744
147E	Alc 1/5A/Rho 83	4.284
104G	Alc 1/5A/Rho 83	2.971
147F	Alc 1/3A/Rho 83	3.100
147G	Alc 1/13X/Rho 83	8.742
147H	Alc 1/NaX/Rho 83	9.510
84G	Alc 1/NaX/Rho 83	12.33
104J	Dythal XL	3.303

As can be seen from the data in Table 5, the combination of hydrotalcite and zeolite exhibits synergism as to VR measurements. In particular, when the zeolite has an average pore size of greater than 5 Angstroms, preferably greater than about 10 Angstroms, exceptionally high VR values are obtained (compare Formulations 141G and 84H with Formulation 84C). In this regard is to be noted that the pore size of NaX zeolite and 13X zeolite are both approximately 13 Angstroms. As can also be seen from the data in Table 5, the stabilizer composition of the present invention provides VR measurements much better than obtained with conventional lead stabilized formulations (see for example Formulation 104J). It can also be seen that the stabilizer composition of the present invention provides better VR values than are obtained with the stabilizer composition disclosed in U.S. Patent 4,427,816 (compare for example Formulations 147C, 141C and 84E with Formulations 141G and 84H). It can also be seen that the incorporation of a beta-diketone into the stabilizer compositions of the present invention can provide enhanced VR values (see for example Formulation 147G, 147H, and 84G).

The data above clearly demonstrates that by using the stabilizer composition of the present invention, one can formulate halogen-containing polymeric formulations which do not use lead stabilizers but which possess thermal stability equivalent to such lead containing formulations. Moreover, the polymeric formulations using the stabilizer compositions of the present invention exhibit electrical properties equal to or superior to those obtained using lead based stabilizers.

The foregoing disclosure and description of the invention is illustrative and explanatory thereof, and various changes in the composition may be made within the scope of the appended claims without departing from the spirit of the invention.

What is claimed is:

1. A stabilizer composition for use in halogen-containing polymers comprising

a hydrotalcite having the general formula:

$$Mg_{1-x}Al_x(OH)_2A_{x/2}.mH_2O$$

wherein x is a number from 0 to 0.5, A is CO_3^{--} or SO_4^{--} and, m is a number representing the number of H_2O in the molecule and, a molecular-sieve zeolite having the general formula:

$$M_{2/n}0.Al_20_3.ySi0_2wH_20$$

wherein M is a cation of a metal selected from Group 1 A and Group II A elements, y is 2 or greater, n is the cation valence, and w represents the water contained in the voids of the zeolite,

the ratio Si/Al in said zeolite being greater than about 1, the weight ratio of hydrotalcite to zeolite being from about 0.5 to 1 to about 3 to 1.

2. The composition of Claim 1 wherein said zeolite has an average pore size of greater than about 5 Angstroms.

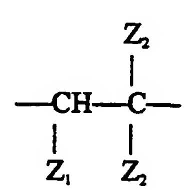
3. The composition of Claim 1 including a beta-diketone.

4. The composition of Claim 1 wherein M is sodium.

5. The composition of Claim 1 wherein said hydrotalcite has the formula:

$$Mg_{0.67}Al_{0.33}(OH)_2(CO_3)_{0.16}0.5H_2O$$

6. A polyvinyl halide resin composition comprising a polyvinyl halide resin formed at least in part of the recurring group:



and having a halogen content in excess of 40 percent by weight and wherein Z_1 is halogen and Z_2 is either hydrogen or halogen, and an effective amount of a stabilizer composition according to Claim 1.

7. The polyvinyl halide resin composition of Claim 6 in which the polyvinyl halide resin is polyvinyl chloride homopolymer.

8. The polyvinyl halide resin composition of Claim 7 in which the polyvinyl halide resin is a copolymer of vinyl chloride and a copolymerizable monomer.

9. The polyvinyl halide composition of Claim 6 wherein said stabilizer composition is present in an amount of from about 0.5 to about 10 parts per hundred parts of resin.

10. The polyvinyl halide composition of Claim 6 wherein said stabilizer composition includes a beta-diketone.

INTERNATIONAL SEARCH REPORT

I... ..ational application No.
PCT/US93/01686

A. CLASSIFICATION OF SUBJECT MATTER
IPC(5) :C08K 5/07, 3/34
US CL :252/400; 524/257, 436, 437
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
[redacted]

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A,	US,A, 4,427,816 (AOKI ET AL) 24 January 1984. See the Abstract.	3 and 10
A	US,A, 4,000,100 (BALDYGA) 28 December 1976. See the Abstract.	1, 2, 4-9
A, P	US,A, 5,106,898 (NOSU ET AL) 21 April 1992 See Col. 1, line 1 through Col. 2, line 2.	1, 2, 4-9
A	US,A, 5,004,776 (TADENUMA ET AL) 02 April 1991, see Col. 1, line 1 through Col. 5, line 42.	1-10
A	US,A, 4,371,656 (KASHIWASE ET AL) 01 February 1983. See Col. 1, through Col. 6, line 33.	1-10

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

* Special categories of cited documents:

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Date of the actual completion of the international search	Date of mailing of the international search report
22 APRIL 1993	25 MAY 1993

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP,A, 57-177033 (KOSEI KK, NIPPON CHEM IND KK) 30 October 1982. See Abstract.	1, 2, 4-9
A	JP,A, 54-34356 (MIZUSAWA KAGAKU KOG) 13 March 1979. See Abstract.	1, 2, 4-9
A	EP,A, 0 332 514 (M & T CHEMICALS, INC.) 13 September 1989.	1, 2, 4-9